Preliminaries for Ch. 7

The Central potential (From Classical Mechanics)

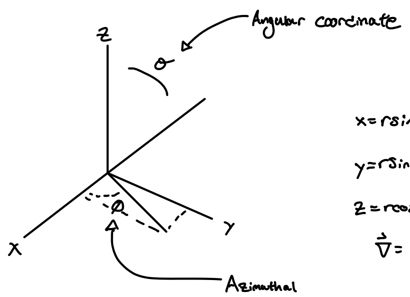
$$V(\vec{r}) = \frac{1}{4\pi\varepsilon_0\varepsilon_n}\frac{e^2}{r}$$

no torque, no change in angular momentum

$$\vec{\nabla} = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

$$\vec{\nabla}\cdot\vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \equiv \nabla^2$$ Laplacian in Cartesian coordinates

Hydrogen Atom



$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\vec{\nabla}\cdot\vec{\nabla} = \nabla^2 = \frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\phi^2}\right]$$

Key Assumptions

1) 1st Approximation ignores nuclear motion
2) Ignore intrinsic angular momentum (spin)
   (only orbital L)
3) This means (@ first) we're ignoring magnetic effects
4) Relativistic effects are ignored

(↳ From last week, keep in mind for any central potential, $\tau = r\times F = 0 \Rightarrow \frac{dL}{dt} = 0$

Seperability of Solutions

Simplest looking way to write Schrödinger wave equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{\mathcal{H}}\Psi \quad w/ \quad \hat{\mathcal{H}} = \frac{-\hbar^2}{2\mu}\nabla^2 + V(r) \quad : \mu = \frac{m_1 m_2}{m_1+m_2}$$

↳ Here we have the coulomb potential

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$\Psi = \psi(r,\theta,\phi)F(t) \qquad f_n(t) = e^{iE_n t/\hbar}$$

$$\hat{\mathcal{H}}\psi_n = E_n\psi_n$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi_n = [E_n - V(r)]\psi_n$$

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \Longrightarrow$$

1) The radial Equation (Laguerre)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V - \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R = 0$$

2) The angular equation:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[\ell(\ell+1) - \frac{m_\ell^2}{\sin^2\theta}\right]\Theta = 0$$

3) The azmuthal equation:

$$\frac{d^2\Phi}{d\phi^2} = -m_\ell^2\Phi \Rightarrow \Phi \sim e^{\pm i m_\ell \phi}$$

Together the product $\Theta(\theta)\Phi(\phi) \equiv Y_{\ell m}(\theta,\phi)$

Spherically Symmetrical Solutions

$\ell = 0 \quad (m_\ell = 0)$

Called 's' states (For "spherically symmetric")

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR_0}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V\right]R_0 = 0$$

$$\frac{1}{r}\frac{d^2}{dr^2}(rR_0) + \frac{2\mu}{\hbar^2}\left[E - V\right]R_0 = 0$$

Scaled Charge

$q_e = \sqrt{\frac{1}{4\pi\epsilon_0}}\, e$

Dimensionless Radians

$\rho = \frac{\mu q_e^2}{\hbar^2} r$

Scaled E

$\epsilon = \frac{2\hbar^2}{\mu q_e^4} E$

Re-Scale & also multiply both sides by ℓ

$$\frac{d^2(\rho R_0)}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho}\right)\rho R_0 \longrightarrow f'' = -\left(\epsilon + \frac{2}{\rho}\right) f_1$$

$f_1 = \rho R_0$

$\psi \xrightarrow[\infty]{r} 0 \longrightarrow f_1 \xrightarrow[0]{\rho} 0$

(must be Finite & Bounded @ origin)

$f_1 = g(\ell)e^{-\alpha\rho}$

$f' = -\alpha e^{-\alpha\rho} g + g' e^{-\alpha\rho}$

$f'' = \alpha^2 e^{-\alpha\rho} g - \alpha e^{-\alpha\rho} g' + g'' e^{-\alpha\rho} - \alpha g' e^{-\alpha\rho}$

α: A free parameter which we may choose to be

$\alpha^2 = -\epsilon$

$g'' - 2\alpha g' + \alpha^2 g = -\left(\epsilon + \frac{2}{\rho}\right) g$

$g'' - 2\alpha g' + \left(\alpha^2 + \epsilon + \frac{2}{\rho}\right) g = 0$

$g'' - 2\alpha g' + \frac{2}{\rho} g = 0$

Power Series:

$g(\rho) = \sum_k^\infty a_k \rho^k$

$g'(\rho) = \sum_k k a_k \rho^k$

$g''(\rho) = \sum_k (k-1) k a_k \rho^{k-2}$

$$\sum_k^\infty k(k-1) a_k \rho^{k-2} - 2\alpha \sum_k^\infty k a_k \rho^{k-1} + 2\sum_k^\infty a_k \rho^{k-1} = 0$$

$$\sum_{k=1}^\infty k(k-1) a_k \rho^{k-2} = \sum_{k=1}^\infty (k+1) k a_{k+1} e^{k-1}$$

$$\sum_{k=1}^\infty \left[(k+1)k a_k - 2\alpha k a_k + 2a_k\right] e^{k-1} = 0$$

$(k+1)(k) a_{k+1} - 2\alpha k a_k + 2a_k = 0$

$a_{k+1} = \frac{2(\alpha k - 1)}{k(k+1)} a_k$

$a_{k+1} = \frac{2(k/n - 1)}{k(k+1)} a_k \qquad \alpha = 1/n$

Bound States: $-\epsilon = 1, \frac{1}{4}, \frac{1}{9}, \frac{1}{16}$

$$E_n = -\frac{\mu q_e^4}{2\hbar^2}\frac{1}{n^2} = \frac{-\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2}\frac{1}{n^2} = \frac{-\hbar^2}{2\mu a_0}\frac{1}{n^2}$$

Bohr radius

For $\ell = 0$ Case:

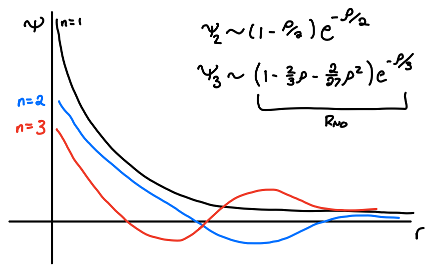
$\psi_n = \frac{g_n(\rho)}{\rho} e^{-\rho/n}$

$g(\rho) = \sum_{k=1}^n a_k \rho^k \qquad$ w/ $\quad a_{k+1} = \frac{2(k/n - 1)}{k(k+1)} a_k$

$\psi_1 \sim e^{-\rho}$

$\psi_2 \sim (1 - \rho/2) e^{-\rho/2}$

$\psi_3 \sim \underbrace{\left(1 - \tfrac{2}{3}\rho - \tfrac{2}{27}\rho^2\right)}_{R_{n0}} e^{-\rho/3}$



Angular Equation

$\Theta \sim P_\ell^{(m)}(\cos\theta)$

Azimuthal Solutions

$\Phi \sim e^{\pm i m_\ell \phi}$

The product of solutions to the angular & azimuthal equations

$Y_{\ell m}(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad \leftarrow$ The spherical harmonics

$Y_{\ell m}(\Omega) \qquad$ typically normalized

Ex : we can show that $Y_{22}(\theta,\phi)$ satisfies the legendre equation:

$l=2$, $m=2$ $\quad Y_{22}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\phi}$

$= c\sin\theta$

$$\frac{dY_{22}}{d\theta} = 2c\sin\theta\cos\theta$$

$$\frac{d^2Y_{22}}{d\theta^2} = 2c[\cos^2\theta - \sin^2\theta]$$

Angular Equation:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{dY_{22}}{d\theta}\right] + \left[2(3) - \frac{4}{\sin^2\theta}\right]Y_{22} = 0$$

$$\frac{1}{\sin\theta}\left[\cos\theta\frac{dY_{22}}{d\theta} + \sin\theta\frac{d^2Y_{22}}{d\theta^2}\right] + \left[6 - \frac{4}{\sin^2\theta}\right]c\sin^2\theta = 0$$

$$\frac{1}{\sin\theta}\left[\cos\theta(2\sin\theta\cos\theta) + 2\sin\theta(\cos^2\theta - \sin^2\theta)\right] + 6\sin^2\theta - 4 = 0$$

$$\cos^2\theta + \cos^2\theta - \sin^2\theta + 3\sin^2\theta - 2 = 0$$

$$2\cos^2\theta + 2\sin^2\theta - 2 = 0$$

$$0 = 0 \quad \checkmark$$

Eigen Functions

$$Y_{nlml}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

$$E_n = -E_0/n^2$$

Solutions to Schrodinger: $\Psi_{n,l,m_l}(r,\theta\phi,t) = \Psi_{n,l,m_l}(r,\theta,\phi)e^{-iE_nt/\hbar}$

n	l	R_{nl}
1	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\cdot\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{a_0^{3/2}}\frac{2}{81\sqrt{3}}\left(27 - r/a_0 + 2\,r^2/a_1^2\right)e^{-r/3a_0}$
3	1	$\frac{1}{a_0^{3/2}}\frac{4}{81\sqrt{6}}\left(6 - r/a_0\right)r/a_0\, e^{-r/3a_0}$
3	2	$\frac{1}{a_0^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

3 Quantum Numbers for 3 Degrees Of Freedom

n: Principal Quantum # $\qquad n = 1, 2, 3 \dots (\infty)$ → unbound

l: Orbital Angular momentum # $\qquad l < n$, $l = 0, 1, 2, \dots\dots, n-1$

m_l: Magnetic Quantum # $\qquad m_l = -l, l+1, \dots\dots l$, $|m_l| \le l$

Ex: For $n=4$, what is the degeneracy (Total # of States w/ same E)

$l = 0, 1, 2, 3$

$m_l = 0$ $\quad m_l = -1, 0, 1$ $\quad m_l = -2, -1, 0, 1, 2$ $\quad m_l = -3, -2, -1, 0, 1, 2, 3$

$|L| \rightarrow l \qquad L = \sqrt{l(l+1)}\,\hbar \qquad$ Bohr model : $n\hbar$

$l=$	0	1	2	3	4	5
	s	p	d	f	g	h

m_l : $\sim L_z = m_l\hbar$ $\quad$ z-component of angular momentum

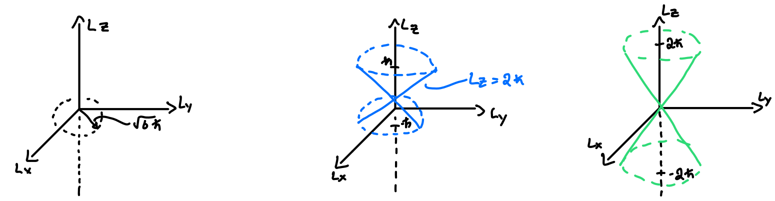
$R_{n0}(r)$

For Spherically Symmetric : $\sim \left(\sum_k^n a_k r^{n-1}\right)e^{-r/na_0}$

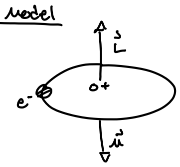
$$\Psi_{n,l,m_l}(r,\theta,\phi) = R_{nl}(r)Y_{l,m_l}(\theta,\phi)$$

Radial (Energy)

$\ell = 2 \qquad L = \sqrt{6}\,\hbar$



Bohr Model

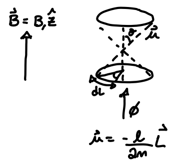


Magnetic moment of atom $\vec{\mu} \Rightarrow \vec{\mu} = -\frac{e}{2m}\vec{L}$

$V_{INT} = -\vec{\mu}\cdot\vec{B} \leftarrow$ Interaction energy

$\vec{\tau} = \vec{\mu}\times\vec{B} \leftarrow$ Torque

If $\vec{\mu}$ is not $\parallel$ to $\vec{B}$, then we get precession about $\vec{B}$.



$\tau = \frac{dL}{dt} = \vec{\mu}\times\vec{B} = \mu B \sin\theta \qquad L_z = m_\ell\hbar \longrightarrow \mu_z = m_\ell\left(\frac{e\hbar}{2m}\right)$

$\frac{dL}{dt} = L\sin\theta\frac{d\phi}{dt} = L\sin\theta\,\omega_L$

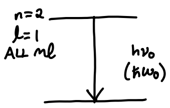
$\omega_L = \frac{1}{L\sin\theta}\frac{dL}{dt} = \frac{\mu B}{L} = \frac{eB}{2m} \qquad w/\ L = \frac{2\mu m}{e}$

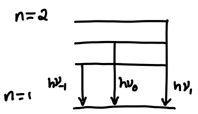
$V_{INT} = -\vec{\mu}\cdot\vec{B} = -\mu_z B = \mu_e m_\ell B$

So Comparing Energy Levels:

2p $\quad n=2,\ \ell=1,\ m_\ell = -1, 0, 1$

No - B-Field $\qquad$ **B-Field $\vec{B} = B_0\hat{z}$**

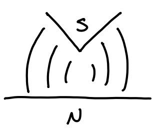




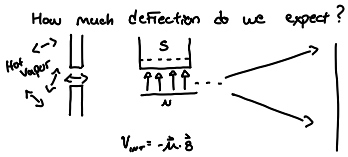
w/ $\quad h\nu_1 > h\nu_0 > h\nu_{-1}$

$(\lambda_1 < \lambda_0 < \lambda_{-1})$

STERN - Gerlach Experiment to Intrinsic Angular Momentum



How much deflection do we expect?



$V_{INT} = -\vec{\mu}\cdot\vec{B}$

$F_z = -\frac{dV}{dz} = \mu_z\frac{dB}{dt} \qquad \mu_z = -\mu_B m_L$

$\mu_B = \frac{e\hbar}{2m}$

$z(t) = \frac{1}{2}a_z t^2 = \frac{1}{2}\left(\frac{F_z}{m}\right)t^2 = \frac{1}{2}\left(\frac{F_z}{m}\right)\left(\frac{\Delta x}{v}\right)^2$

$= \frac{1}{2}\frac{1}{m}\left(\mu_z\frac{dB}{dz}\right)\left(\frac{\Delta x}{v}\right)^2$

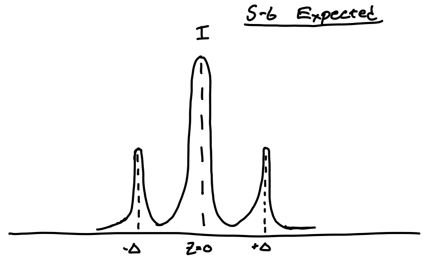
$= \frac{1}{2m}\left(-\mu_B m_\ell\frac{dB}{dz}\right)\left(\frac{\Delta x}{v}\right)^2$

$Z(t) = -\left[\frac{\mu_B}{2m}\frac{dB}{dz}\left(\frac{\Delta x}{v}\right)^2\right]m_\ell$

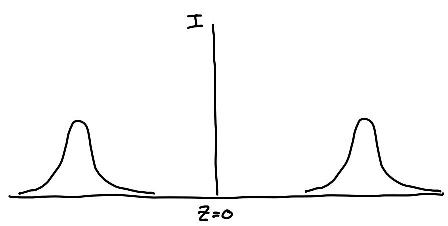
If n=1: $\quad \ell < n \Rightarrow \ell = 0 \Rightarrow$ No deflection
$(|m_\ell|) \le \ell = 0$

If n=2: $\quad \ell = 1 \ \left\{ \begin{array}{l} m_\ell = 1 \\ m_\ell = 0 \\ m_\ell = -1 \end{array} \right.$
$\ell = 0$

S-G Expected



Actual S-G



Goudsmit & Uhlenbeck: Intrinsic angular momentum of Electron w/ value $|S| = \frac{1}{2}$ for the z-component.

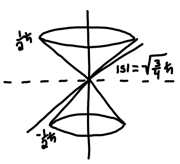
$\longrightarrow \pm\frac{1}{2}$, Fermions all have this

Spin $\frac{1}{2}$ (Fermion) Details

Spin acts like orbital angular momentum w/ 2 allowed S_z values for Fermions. The total Magnitude:

$|\vec{S}| = \sqrt{s(s+1)}\,\hbar = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \sqrt{\frac{3}{4}}\,\hbar$

So Graphically:



$\vec{\mu}_S = -\frac{e}{m}\vec{S} = \underbrace{-\frac{2\mu_B}{\hbar}}_{\text{Factor of 2 from relativity}}\vec{S}$

compare with orbital τ:

$\vec{\mu}_L = -\frac{\mu_0 L}{\hbar}, \quad V_{INT} = -\vec{\mu}_S\cdot\vec{B} = e/m\,\vec{S}\cdot\vec{B}$

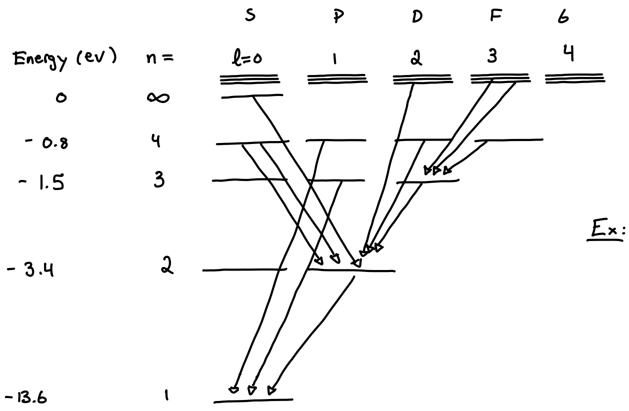
The state of the H-atom is completely specified by the 4 Quantum #'s:

$n \Rightarrow$ Integer 1 to ∞ (Radial F_n, E_n)

$\ell \Rightarrow$ Integer $< n$ (Angular #, orbital $\vec{L}$)

$m_\ell \Rightarrow$ Integer $|m_\ell| \le \ell \Rightarrow$ Azimuthal, (Magnetic) #, specifies $L_z/\hbar$

$m_s \Rightarrow = \pm\frac{1}{2} \Rightarrow$ Spin #, specifies z-component of $\vec{S}$ where $\vec{S}$ is the intrinsic angular momentum of e^-.



$\Delta n =$ Anything

$\Delta l = \pm 1$ (Dipole Selection)

$\Delta m_l = 0, \pm 1$ (No conditions on m_s for a 1-Electron Atom)

<u>Ex:</u> $\underset{n\ l\ m_l\ m_s}{(2,0,0,\tfrac{1}{2})} \Rightarrow (3,1,1,\tfrac{1}{2})$

$\Delta E = -\frac{E_0}{n'^2} - \left(-\frac{E_0}{n^2}\right) = -E_0\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$

$\Delta l = 1$, $\Delta m_l = 1$ $\Rightarrow$ Allowed

$\Delta E = -E_0\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = \frac{5}{36}E_0 \geq 0$

$$P(\vec{r},\theta,\Phi,t)\,dr = \Psi^*(r,\theta,\phi,t)\Psi(r,\theta,\phi,t) = |\Psi|^2$$

$$\Psi_{n,l,m_l,m_s} = rR_{nl}(r)\Psi_{lm}(\theta,\phi)$$
$$\Psi_{lm} = (\cos\theta)e^{im\phi}$$

Probability of a particle in a region Ω: $\int_\Omega P(r,\theta,\phi)\,d\Omega$

w/ $d\Omega = r^2 \sin\, dr\,d\theta\,d\phi$

$P(r)dr \equiv$ Prob. of Finding e^- in r to $r+dr$ (At any θ,ϕ)

$= [r^2 R_{nl}^2(r)] \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} Y_{lm}^*(\theta,\phi)Y_{lm}(\theta,\phi)\,d\phi$

<u>Ex:</u> $n=3, l=2$, what is the most probable radius?

$$R_{32}(r) = \frac{1}{a_0^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$$

$$P_{32}(r)\,dr = \left(\frac{1}{a_0^{3/2}}\frac{4}{81\sqrt{30}}\right)^2 \frac{r^6}{a_0^4}e^{-2r/3a_0}\,dr$$

$$\frac{dP_{32}}{dr} = 0 \Rightarrow (\quad)^2 \frac{d}{dr}\left[\frac{r^6}{a_0^4}e^{-2r/3a_0}\right] = 0$$

$$6 - \frac{2r}{3a_0} = 0 \Rightarrow r_{max} = 9a_0$$

$$P(r \leq a_0) = \int_0^{a_0} P_{32}(r)\,dr = (\quad)\int_0^{a_0} r^6 e^{-2r/3a_0}\,dr$$

$$\frac{d}{d\beta}\int e^{\beta x}\,dx = \int x e^{\beta x}\,dx$$

$$\frac{d}{d\beta}\int x e^{\beta x}\,dx = \int x^2 e^{\beta x}\,dx$$

<u>Probability & Expectation Value Integral Tricks</u>

$$P_{ab} = \int_a^b dr\,P_{nl}(r) = \int_a^b r^2 R_{nl}^2(r)\,dr$$

Probabilities of e^- in some Region (Specified State, Normalized ψ, and here integrating over all angular parts)

R_{nl}'s are polynomials of degree r^{n-1} multiplied by e^{-r/na_0}

$H_n(\xi)$ have definite parity

So the $P_{nl}(r) \sim \left(\sum_{k=1}^{2n+1} \alpha_k r^k\right)e^{-2r/na_0}$

$\therefore P_{ab} = \int_a^b r^2 R_{nl}^2(r)\,dr = \sum_k^{2n+1}\alpha_k\left[\int_a^b r^k e^{-2r/na_0}\,dr\right]$

$$I = \int x^n e^{ax}\,dx = \frac{e^{ax}}{a^{n+1}}\left[(ax)^n - n(ax)^{n-1} + n(n-1)(ax)^{n-2} - \dots + (-1)^n n!\right]$$

<u>Notice:</u> You can do this (Sometimes more useful)

$$\frac{\partial}{\partial x}\left[\int x^{n-1}e^{ax}\,dx\right] = \int x^n e^{ax}\,dx$$

We can do this for infinite intervals or finite ones:

Ex: Calculate $\langle r \rangle$ & $\langle r^2 \rangle$ for the $n \geq 2$, $\ell = 1$

State of the Hydrogen atom.

$$\psi_{21} \rightarrow R_{21}(r) = \frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$$

$$\langle r \rangle = \int_0^\infty r\left(r^2 R_{21}^2(r)\right) dr = \int_0^\infty r\left[r^2\left(\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}\right)^2\right] dr = \left(\frac{1}{a_0}\frac{1}{\sqrt{3}(2a_0)^{3/2}}\right)^2 = \underbrace{\int_0^\infty r^5 e^{-r/a_0} dr}_{I}$$

$$I = \int_0^\infty x^n e^{-ax} dx = \begin{cases} \dfrac{\Gamma(n+1)}{a^{n+1}} & n > -1,\ a > 0 \\ \dfrac{n!}{a^{n+1}} & n\text{- integer},\ a > 0 \end{cases}$$

$\Gamma(z+1) = \Gamma(z)$ → Gamma Function

$$\langle r \rangle = \frac{1}{24 a_0^5}\left(5!\, a_0^6\right) = 5a_0$$

$$\langle r^2 \rangle = \left(\frac{1}{24a_0^5}\right)\int_0^\infty r^2\left[r^2 R_{21}^2(r)\right] dr = \frac{1}{24a_0^5}\int_0^\infty r^6 e^{-r/a_0} dr = -\left(\frac{1}{24a_0^5}\right)\frac{\partial}{\partial(1/a_0)}\int_0^\infty r^5 e^{-r/a_0} dr$$

α

$$= -\left(\frac{1}{24a_0^5}\right)\frac{d}{d\alpha}\left[\frac{n!}{\alpha^{n+1}}\right] = \left(\frac{1}{24a_0^5}\right)\frac{5!(n+1)}{\alpha^{n+2}} = \frac{5!(6)}{4!} = 30a_0^2$$

$$\langle r^2 \rangle = 30a_0^2$$

For Exam 3

- Degeneracy Problem (Like #8)
- Zeeman Splitting - or - Stern-Gerlach Problem (Like #1 or 2)
- understanding how $\ell \leftrightarrow |\hat{L}|$ & $m_\ell \Leftrightarrow L_z$ relate algebraically & graphically. (Why can't we have L_x or L_y?)

The Final

3/4 Conceptual Questions Exam 1

3/5 Conceptual Questions Exam 2

3 or Ch. 7 conceptual Questions (Not on Exam 3)

1 Problem (SHO or Hydrogen Atom)